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A SIMPLE AND EFFECTIVE METHOD FOR SYNTHESIS OF NANOSIZED $Ni_{0.5}$ $Cu_{0.5}$ Fe_2O_4 PARTICLES

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ABSTRACT

Nano crystalline nickel-copper ferrites $Ni_{05}Cu_{0.5}Fe_2O_4$ have been synthesized via precipitation method and characterized by using XRD (X-ray diffraction), TGA/DTA (Thermo gravemetric analysis), SEM (Scanning electron microscopy)/TEM (Transmission electron microscopy) and magnetic measurement by using VSM (Vibrating sample magnetometer). The X-ray diffraction patterns confirm the formation of single phase cubic spinel structure. SEM (Scanning electron microscopy) was used to characterize the micro structure of the ferrite samples. A homogenous and fine grain structure was found. By using TEM (Transmission electron microscopy) particle size was calculated. The particle size of synthesized $Ni_{05}Cu_{0.5}Fe_2O_4$ varied from 8.2758 nm to 41.6666 nm, which is in good agreement of the theoretically predicted size of nano materials. Magnetic measurements shows that $Ni_{05}Cu_{0.5}Fe_2O_4$ is super paramagnetic in nature at room temperature and hence used in magnetic devices. This method is easier, more effective and convenient in comparison to the known methods of the synthesis of $Ni_{05}Cu_{0.5}Fe_2O_4$ nano materials like combustion synthesis, chemical vapour deposition technique, hydro thermal synthesis, dip coating technique, conventional ceramic method, pulsed laser technique, spray pyrolysis, sputtering and thermal cracking.

Key words: Nano crystalline, Spinel ferrites, Super paramagnetic, Nickle-copper ferrite ($Ni_{05}Cu_{0.5}Fe_2O_4$).

INTRODUCTION

Ni-Cu ferrites are magnetic materials with improved magnetic, high resistance and high frequency response. Several researchers have focused their research on Ni-Cu ferrite because copper containing ferrites because copper constraining ferrites have interesting electrical and magnetic properties[1-4]. Magnetic materials are mainly of two type; soft magnetic materials and hard magnetic materials. A soft magnet has obvious magnetism only when it is in magnetic field[5]. A hard magnet retains obvious magnetism permanently and they are permanent magnets[6]. Metal oxide spinel ferrites have proved to be very important for catalysis and very important for catalysis and ferrites obtained by combustion synthesis

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show application in biodiesel production[7,8], which is a renewable source of energy largely used for substitution of fossil fuels[9]. Ferrites are widely used in different electrical engineering applications including carrier telephony in inductors, TV sets, transformers in radio as diode, transistor and solar cell[10]. Ni-Cu ferrites have critical need for high frequency applications such as magnetic sensors, rod antennas, transformer cores, telecommunication and microwave devices[11-16]. In advanced materials, ferrites are most widely used magnets comprising 52% of the world market[17]. Old methods of synthesis of ferrites are hydrothermal synthesis[18], conventional ceramic method[19] and thermal cracking[20,21]. Snoek[22] worked on the advancement of high frequency ferrite and found high frequency range of ferrites.

Along with a number of research workers engineers are also involved in improvement and application of ferrites. Various techniques are used for synthesis of ferrites, which include chemical vapour deposition technique[23], pulsed laser deposition technique[24] and ferrite plating[25].

There is great need to establish facilities for the preparation and characterization of such advanced materials. The present work is an attempt to the goal. The present study aims to prepare $Ni_{05}Cu_{0.5}Fe_2O_4$ by using aqueous precipitation method, which is comparatively of low cost with improved magnetic and electrical properties. The crystallite size and microstructure of the prepared ferrite are investigated by XRD (X-ray diffraction), TGA/DTA (Thermo gravimetric analysis), SEM (Scanning electron microscopy)/TEM (Transmission Electron Microscopy) and Magnetic measurements by using VSM (Vibrating Sample Magnetometer).

EXPERIMENTAL

Methods and materials

Chemicals

All chemicals used in the experiment were of analytic reagent grade. Fe $(NO_3)_3$, Cu $(NO_3)_2$, Ni $(NO_3)_2$ and liquor ammonia were purchased from Merck, India. Deionized water was used throughout the experiment.

Synthesis of $Ni_{0.5}Cu_{0.5}Fe_2O_4$

200 mL of 0.5 M solution of $Zn(NO_3)_2$ was mixed with 200 mL of 0.5 M solution of $Cu(NO_3)_2$ and 200 mL of 0.5 M solution of $Ni(NO_3)_2$; then aqueous ammonia was added drop wise with constant stirring until the pH of the solution reached to 10. The precipitate thus obtained were filtered on buckner funnel and washed several times with distilled water.

The precipitate were dried in oven at 70°C for 24 hrs and were calcined at 600°C in a muffle furnance for 5 hours. Obtained material was ground and sieved through 100 mesh size sieve.

Equipments

An X-ray measurement was carried out using X-ray diffractometer system Philips PW 11/90, with nickel filtered CuKα (l = 1.5405 Å).

The crystalline size of Zinc ferrite was calculated using Scherrer equation.

$$d = K\lambda/ \beta \cos \theta$$

Where d is the average crystallite size of the phase under investigation, K is the Scherrer constant (0.89), λ is the wave length of X-ray beam used, β is the full-with half maximum(FWHM) of diffraction (in radians) and θ is the Bragg's angle.

Transmission electron micrograph (TEM) were recorded on Hitachi H7500. The samples were dispersed in ethanol and then treated ultrasonically in order dispersed individual particles over a gold grid. The surface morphology of $Ni_{05}Cu_{0.5}Fe_2O_4$ prepared by precipitation method was investigated by using scanning Electron Microscope Quanta 200 FEG (FEI Netherlands).

The magnetic properties of the solid was measured at room temperature using a vibrating sample Magnetometer Model 155.

RESULTS AND DISCUSSION

X-ray studies

The X-ray diffraction pattern of synthesized $Ni_{05}Cu_{0.5}Fe_2O_4$ nano particles is depicted in Fig. (1). X-ray diffraction pattern of $Ni_{05}Cu_{0.5}Fe_2O_4$ pure indicated that Ni-Cu ferrite in the form of $Ni_{05}Cu_{0.5}Fe_2O_4$ (Fig. 1). In X-ray diffraction, some prominent peaks were considered and corresponding d-values were compared with the standard i.e. JCPDS (Joint Committee on Powder Diffraction Standards) (File No. 25-0283) (Table 1). X-ray diffraction shows that metal oxide is pure $Ni_{05}Cu_{0.5}Fe_2O_4$ having cubic spinal structure formation of single phase spinel ferrite with crystalline size between 18-34 nm. The average crystallite size was determined from the broadening of the most intense peaks using Debye Scherer equation (Cullity 2001) and values shown in Table 1 and it also supports the SEM/TEM observations. The crystallite six was found within 16-29 nm. The powder x-ray patterns confirm the single phase spinel structure for synthesized material. Thickness of the crystal has been calculated using Debye Scherrer's formula and it support the TEM observations.

Table 1: X-ray diffraction data for $Ni_{05}Cu_{0.5}Fe_2O_4$

S. No.	d = λ / 2sinθ (Observed)	d = λ / 2sinθ (Reported)	I/I_0 x 100% (Observed)	I/I_0 x 100% (Reported)
1	19.079	19.079	57.0568	57.0570
2	20.532	20.531	99.99997	99.99999
3	21.865	21.861	27.22720	27.22722
4	28.117	28.118	27.92791	27.92792
5	32.696	32.696	10.71069	10.71071
6	35.925	35.925	10.71068	10.71071
7	42.559	42.557	8.00799	8.00800
8	61.761	61.759	3.70369	3.70370
9	74	74	3.70369	3.70370

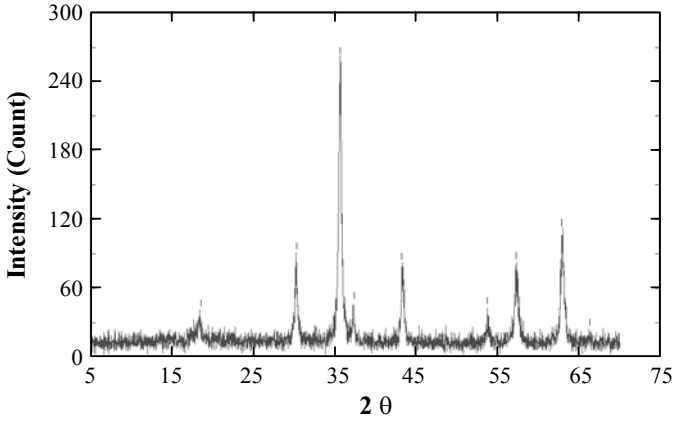


Fig. 1: X-Ray diffraction spectra of $Ni_{05}Cu_{0.5}Fe_2O_4$ Particles

Thermal analysis

Thermal analysis includes a group of techniques in which a physical property of a substance is measured as a function of temperature or time while the substance is subjected to a controlled temperature programme. The analysis involves thermogravity (TG), differential thermal analysis (DTA) and derivative Thermogravimetry (DTG). Thermal gravimetric studies of the calcined oxides prepared were done between a temperature range of 10-1000^oC under N_2 atmosphere. The TGA/DTA curves of the oxides are shown in Fig. 2. The maximum total weight loss observed for nickel oxide and their corresponding temperature is summarized in Table 2. Results showed that in the synthesized oxides shows some weight loss and ferrite undergoing decomposition, dehydration or any physical change.

In DTA curve also, there is exothermic peak, which shows phase transition, solid state reach on any chemical reaction occurred during heating treatment.

Table 2: Observations of weight loss for $Ni_{05}Cu_{0.5}Fe_2O_4$ at corresponding temp. range

S. No.	Maximum % loss in weight	Temperature range (^oC)
1	2.027%	26.18-902.64

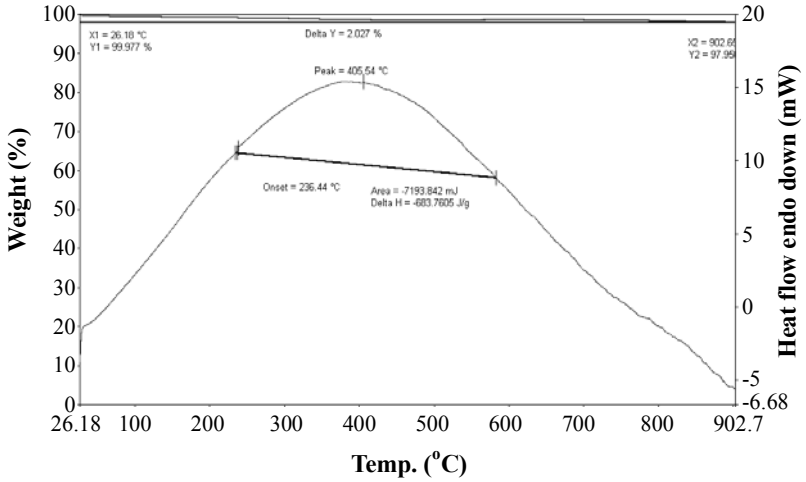


Fig. 2: TGA-DTA of $Ni_{05}Cu_{0.5}Fe_2O_4$ particles

SEM/TEM studies

SEM studies were carried out to study the morphology of the sample Fig. (3a, b) show the SEM micrographs of $Ni_{05}Cu_{0.5}Fe_2O_4$. The micrographs of $Ni_{05}Cu_{0.5}Fe_2O_4$ (Fig. 3a, b) displayed spherical particles with high agglomeration.

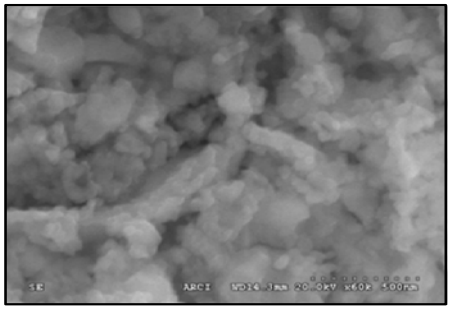


Fig. 3(a): SEM micrographs of $Ni_{05}Cu_{0.5}Fe_2O_4$ particles

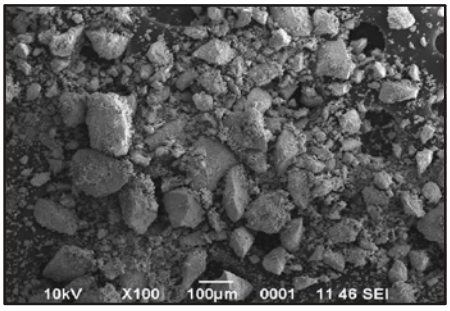
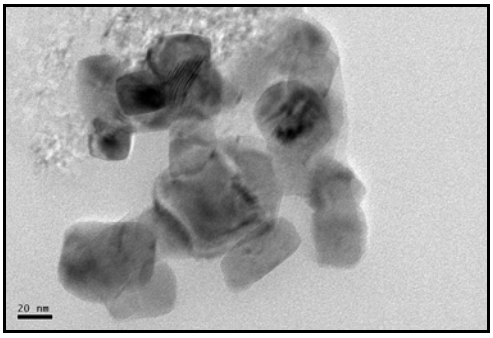
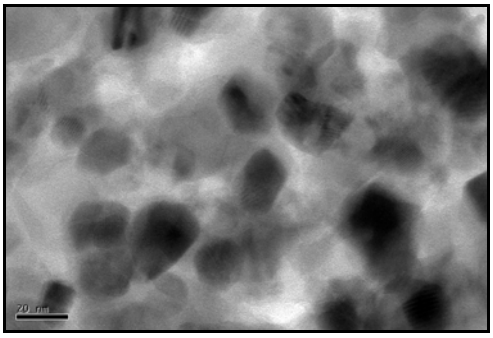


Fig. 3(b): SEM micrographs of $Ni_{05}Cu_{0.5}Fe_2O_4$ particles

TEM studies were carried out to find the exact size of the synthesized $Ni_{05}Cu_{0.5}Fe_2O_4$ nanoparticles Fig. (4a, b, c, d, e, f, g) show the TEM images of the synthesized $Ni_{05}Cu_{0.5}Fe_2O_4$ nanoparticles. It shows that the size of the obtained nano particles is in the range 8.2758-41.6666 nm. Most of the particles are in the range 18-34 nm. TEM images indicate that $Ni_{05}Cu_{0.5}Fe_2O_4$ samples were all spherical particles with uniform grain size distribution.



(a)



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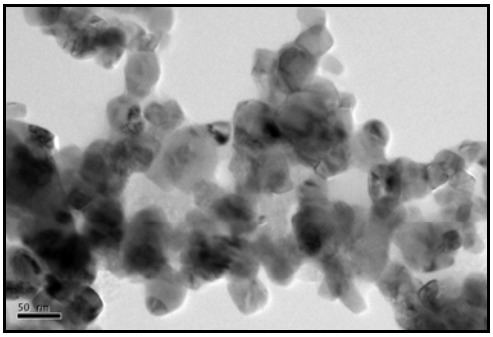

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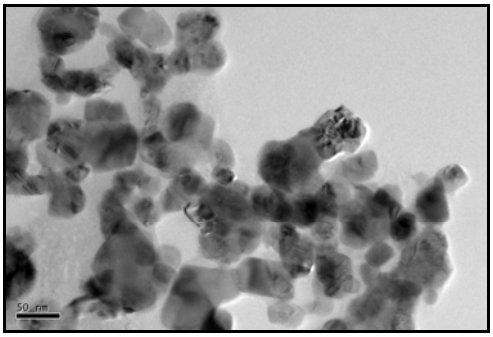

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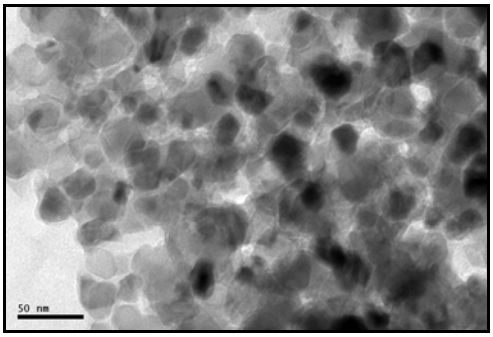

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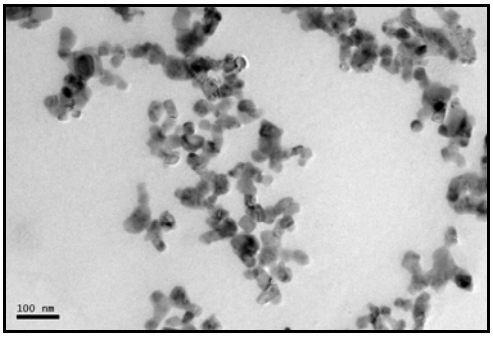

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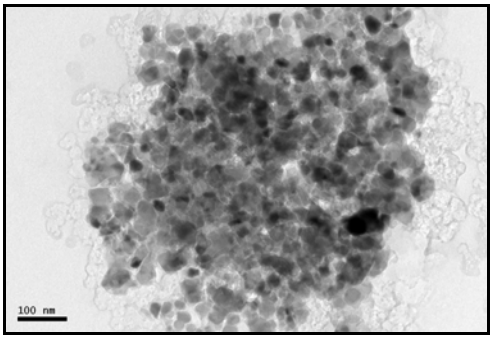


(g)

Fig. 4(a, b, c, d, e, f, g): TEM micrographs of $Ni_{05}Cu_{0.5}Fe_2O_4$ particles

Magnetic measurements

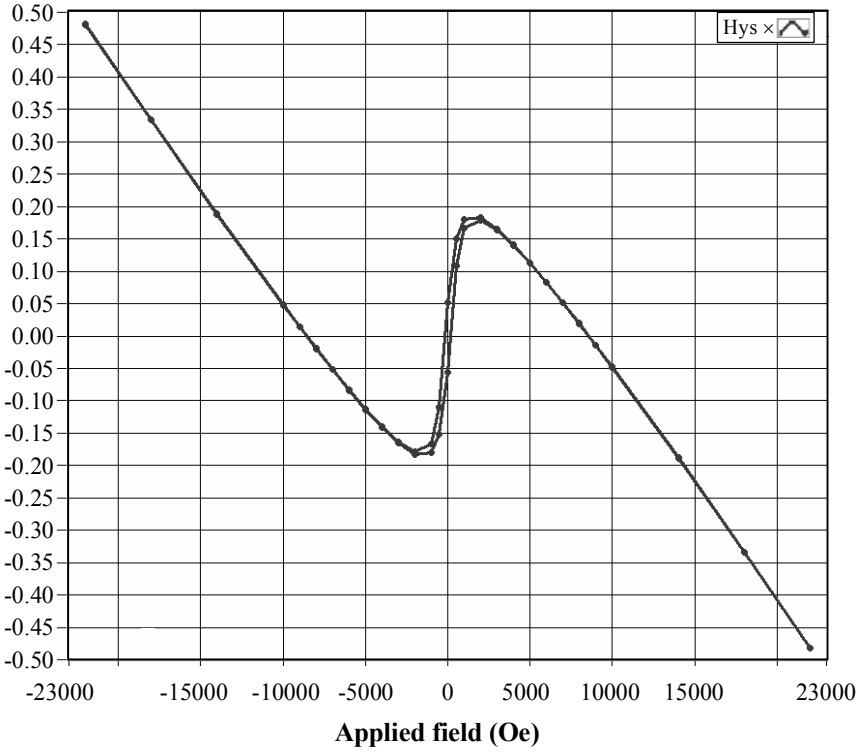
The magnetic measurements of $Ni_{05}Cu_{0.5}Fe_2O_4$ was carried out at room temperature and it has been shown that the magnetic measurements shows that the prepared $Ni_{05}Cu_{0.5}Fe_2O_4$ nanoparticles posses good super paramagnetic behavior at room temperature (300K) with saturation magnetization MS value 52 (Fig. 5). Previously reported values of Ms for $Ni_{05}Cu_{0.5}Fe_2O_4$ nanoparticles prepared by various methods has been reported in (Fig. 5). The value of Ms ranging from 16-89 emu/g shows that Ms strongly depends on the methods of synthesis.

Table 3: Practical size of synthesized $Ni_{05}Cu_{0.5}Fe_2O_4$ at different scales

S. No.	Scale (20 nm)	Scale (20 nm)	Scale (50 nm)	Scale (50 nm)	Scale (50 nm)	Scale (100 nm)	Scale (100 nm)
1	8.2758	34.1666	18.9189	20.2702	29.1666	25	35.7142
2	13.7931	18.3333	27.0270	20.2702	20.8333	21.4285	28.5714
3	17.2413	30.8383	29.7297	20.2702	16.6666	17.8571	28.5714
4	21.3793	34.1666	20.2702	10.8108	18.75	39.2857	25
5	24.1379	22.5	14.8648	20.2702	27.0833	32.1428	25
6	16.5517	18.3333	22.9729	20.2702	31.25	28.5714	21.4285
7	8.2758	30.8383	21.6216	18.9189	12.5	35.7142	17.8571
8	13.7931	34.1666	17.5675	24.3243	25	28.5714	39.2857

Cont…

S. No.	Scale (20 nm)	Scale (20 nm)	Scale (50 nm)	Scale (50 nm)	Scale (50 nm)	Scale (100 nm)	Scale (100 nm)
9	17.2413	22.5	18.9189	20.2702	41.6666	28.5714	32.1428
10	21.3793	18.3333	16.2162	29.7297	20.8333	25	28.5714
Range	8.2758 nm to 24.1379 nm	18.3333 nm to 34.1666 nm	14.8648 nm to 29.7297 nm	10.8108 nm to 29.7297 nm	12.5 nm to 41.6666 nm	21.4285 nm to 39.3857 nm	21.4285 nm to 39.3857 nm



Hysteresis loop	Upward part	Downward part	Average	Parameter definition Hysteresis parameters
Hc Oe	-22003.000	-22000.000	-1.500	Coercive field: Field at which M//H changes sign
Mr emu	-54.986E-3	51.151E-3	53.068E-3	Remanent magnetization: M at H = O
S	0.114	0.106	0.081	Squareness : Mr/Ms
S*	1.063	1.068	1.049	1-(Mr/Hc)(1/slope at Hc)

Fig. 5: Magnetic measurement of synthesized $Ni_{05}Cu_{0.5}Fe_2O_4$ Particles

This Ms value at room temperature is good and comparable with methods of synthesis as thermal decomposition method (Ms value 44 at 300 K and Ms value 69.5 $emug^{-1}$ at 10 k) ball milling (Ms value 19.6 in at 4.2 k) and other co-precipitation routes which shows a maximum Ms 48.2 at 4.2 k (Table 2). Magnetic hysteresis curve clearly indicate the soft nature of the prepared sample saturation magnetization ms value increase with time.

CONCLUSION

$Ni_{05}Cu_{0.5}Fe_2O_4$ nanoparticle with cubic spinel structure are synthesized successfully by aqueous precipitation method. From SEM/TEM studies, it was found that particles have average size 18-34 nm. Magnetic measurements shows that $Ni_{05}Cu_{0.5}Fe_2O_4$ super paramagnetic in nature having saturation magnetization (Ms) value 52 emu/g. This method is advantageous over the existing methods of synthesis of nano particles because other methods require expensive materials, highly skilled labour and specialized instrumentation. Therefore, the proposed precipitation method is easier, cheaper, very promising and may have extensive applications.

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